

PTO 02-3870

CY=JP DATE=19920331 KIND=A  
PN=04-099236

PRODUCTION METHOD OF COPPER CONTAINING VERY LOW OXYGEN  
[Kyokuteisan'sodo no Seizohoho]

Takuro Iwamura, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. August 2002

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	04-099236
DOCUMENT KIND	(12):	A
	(13):	PUBLISHED UNEXAMINED PATENT APPLICATION (Kokai)
PUBLICATION DATE	(43):	04-099236 [WITHOUT GRANT]
PUBLICATION DATE	(45):	[WITH GRANT]
APPLICATION NUMBER	(21):	02-209762
APPLICATION DATE	(22):	19900808
PRIORITY DATE	(32):	
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	
DOMESTIC CLASSIFICATION	(52):	
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTOR	(72):	IWAMURA, TAKUO; FURUYA, TSUGIO; ISHIDA, TOKUKAZU; ASAO, HARUHIKO.
APPLICANT	(71):	Mitsubishi Material K.K.
TITLE	(54):	PRODUCTION METHOD OF COPPER CONTAINING VERY LOW OXYGEN
FOREIGN TITLE	[54A]:	Kyokuteisan'sodo no Seizohoho

## 1. Name of this invention

Production Method Of Copper Containing Very Low Oxygen

## 2. Claims

[1] Production method of copper containing very low oxygen with the following characteristic:

Reductive gas prepared by mixing 0.5 - 50 volume % of H<sub>2</sub> (per total volume) and one or more materials selected from N<sub>2</sub>, Ar, and CO is blown into hot water containing melted pure copper (purity > 99.99%) containing:

Oxygen: 3 - 10 ppm

Hydrogen: 1 ppm or less

to reduce the oxygen and hydrogen contents to

Oxygen: 1 ppm or less

Hydrogen: 0.8 - 3 ppm

Then, the first dehydrogenation process is performed to this deoxidated hydrogen-rich pure copper hot water by providing a reaction gas consisting of one or more materials selected from N<sub>2</sub>, Ar, and CO in order to adjust the oxygen and hydrogen amounts to the following:

Oxygen: 1 ppm or less

---

\*Numbers in the margin indicate pagination in the foreign text.

Hydrogen: 0.5 - 1.5 ppm

After this first dehydrogenated copper hot water is made into an ingot cast, the second dehydrogenation process is performed to the ingot for a certain duration while temperature is maintained at 700 - 900°C in a non-oxidizing atmosphere in order to adjust the oxygen and hydrogen contents to the following:

Oxygen: 1 ppm or less

Hydrogen: 0.3 ppm or less

### 3. Detailed Explanation of this Invention

[Industrial Field]

This invention pertains to a production method of copper containing a very small amount of oxygen [1 ppm or less of oxygen (hereinafter, expressed as "O")].

[Conventional Technology]

To prepare pure copper of at least 99.99% purity, pure copper, deoxidized copper, and vacuumed-dissolved copper are /228 conventionally used. Among those materials, pure copper has a lowest amount of [O], only 3 - 10 ppm of oxygen, providing excellent extension and processing characteristics. Therefore, this material is commonly utilized for producing fine wire used as the bonding wire for semiconductor devices and foil used for semiconductor printed substrates.

#### [Problems to Be Solved by this Invention]

To accommodate the recent high integration of semiconductor devices, bonding wire and printed substrate must be further thinned. However, despite of low amount of oxygen content (3 - 10 ppm) in the copper, even this small amount of oxygen causes sufficient extension and processing characteristics of the product, thereby failing to produce desired thinner devices, since the product is easily disconnected or broken when the device is further thinned. As a result, high production cost is unavoidable.

Although conventional refinement methods, such as vacuum-melting and melting in a CO-included gas atmosphere, are used to refine pure copper, the amount of [O] cannot be made lower than 2 ppm.

#### [Method to Solve the Problems]

To solve those problems, the developers of this invention researched a technique to produce copper containing a smaller amount of [O] than the amount included in the conventional pure copper and discovered the following new method:

Reductive gas prepared by mixing 0.5 - 50 volume % of  $H_2$  (per total volume) and one or more materials selected from  $N_2$ , Ar, and CO is blown into hot water containing melted pure copper (purity > 99.99%) containing:

[O]: 3 - 10 ppm,

Hydrogen (hereinafter, expressed as [H]): 1 ppm or less  
to reduce the oxygen and hydrogen contents to

[O]: 1 ppm or less,

[H]: 0.8 - 3 ppm.

Then, the first dehydrogenation process is performed to this deoxidated hydrogen-rich pure copper hot water by providing a reaction gas consisting of one or more materials selected from N<sub>2</sub>, Ar, and CO, allowing the [H] content to be reduced to 0.5 - 1.5 ppm without affecting the [O] content.

After this first dehydrogenated copper hot water is made into an ingot cast, the second dehydrogenation process is performed to the ingot for a certain duration while temperature is maintained at 700 - 900°C in a non-oxidizing atmosphere in order to adjust the hydrogen content to 0.3 ppm or less without affecting the oxygen amount. The prepared copper containing a very small amount of oxygen can be easily made into an ultra thin wire having a 50 μm diameter, where the diameter of conventional ultra thin wire cannot be made smaller than 60 μm. Furthermore, this copper containing a very small amount of oxygen can be made into a pressure-extended copper foil having a much improved bending characteristic compared with the conventional copper foil.

The method based on this invention was developed according to the discovery described above. That is, this invention provides

the following production method of copper containing a very small amount of oxygen:

Reductive gas prepared by mixing 0.5 - 50 volume % of  $H_2$  (per total volume) and one or more materials selected from  $N_2$ , Ar, and CO is blown into hot water containing melted pure copper (purity > 99.99%) including:

[O]: 3 - 10 ppm,

[H]: 1 ppm or less,

to reduce the oxygen and hydrogen contents to

[O]: 1 ppm or less,

[H]: 0.8 - 3 ppm.

Then, the first dehydrogenation process is performed to this deoxidated hydrogen-rich pure copper hot water by providing a reaction gas consisting of one or more materials selected from  $N_2$ , Ar, and CO to adjust the amounts of [O] and [H] to the following:

[O]: 1 ppm or less,

[H]: 0.5 - 1.5 ppm.

After this first dehydrogenated copper hot water is made into an ingot cast, the second dehydrogenation process is performed to /229 this ingot for a certain duration at 700 - 900°C in a non-oxidizing atmosphere in order to adjust the oxygen and hydrogen contents to the following:

[O]: 1 ppm or less,

[H]: 0.3 ppm or less.

Contents of [O] and [H] in the deoxidated hydrogen-rich pure copper hot water based on this invention can be naturally determined. In other words, the values were determined based on the results of the following experiments: When 3 - 10 ppm of [O] existing in the pure copper material melted hot water is reduced to 1 ppm or less using said reductive gas containing  $H_2$ : 0.5 - 50 volume %, content of [H] can be naturally enriched to 0.8 - 3 ppm. Then, the amount of [H] can be reduced to 0.3 ppm or less from this level of [H] quantity by performing the first and second dehydrogenation processes without increasing the amount of [O].

The reason for setting the ratio of  $H_2$  to 0.5 - 50 volume % in the method based on this invention is that, when the ratio is less than 0.5 volume %, the desired [O] reduction effect cannot be obtained; on the other hand, if the ratio exceeds 50 volume %, the [H] content in the deoxidized hydrogen-rich pure copper hot water exceeds 3 ppm, thereby requiring an uneconomical extensive processing time for reducing such level of [H] to 0.3 ppm or less by the next dehydrogenating process.

The reason for setting the temperature for the second dehydrogenation heating process to 700 - 900°C is that, if the temperature is less than 700°C, required dehydrogenation takes too long time; on the other hand, if the temperature exceeds 900°C, the



crystal particles tend to enlarge, thereby worsening the strength and extension characteristics. As a result, foil material and extremely thin wires tend to cause breakage and disconnection during the production process.

#### [Operational Examples]

The following explains the operational examples of this invention.

Pure copper was used as a raw material and melted in a normal oven to prepare 10 Kg each of pure copper melted hot water containing the amounts of [O] and [H] shown in Table 1. Then, a reductive gas consisting of the materials shown in Table 1 was blown at a ratio of 1 l/min at 1150°C for 10 minutes (first dehydrogenation process) to prepare the first dehydrogenated pure copper containing amounts of [O] and [H] shown in Table 1. Next, this hot water was made into an ingot cast (diameter = 70 mm). To perform the operational examples 1 - 9 and comparison examples 1 - 9, the second dehydrogenation heat process was applied to this ingot under the conditions shown in Table 1 (holding time = 60 minutes). As a result, coppers containing fairly low oxygen quantities (operational examples 1 - 9) and coppers containing relatively low amounts of oxygen (comparison examples 1 - 9) were prepared. Their purity levels and contents of [O] and [H] are shown in Table 2.

Although a batch method was used in those examples in order to clarify the variation of each process, a continuous method is preferred in the practical operation. That is, to produce the extremely low oxygen copper, ingots should be successively produced from a continuous refinement device comprised of the following parts before applying the second dehydrogenation process: A continuous air-tight refinement device which is air-shielded and connected to an oven for melting pure copper, deoxidization device which blows a reductive gas to the pure copper melted hot water to cause reaction with the oxygen in the hot water while removing oxygen, dehydrogenation device which blows a reaction gas to the deoxidized hydrogen-rich pure copper hot water or exposes the water to the reaction gas to perform the first dehydrogenation process, and continuous casting device for casting the copper hot water using a melted hot water path sealed by the air-tight hot water path.

Note that Comparison examples 1 - 9 were performed under the assumption that one of production conditions (indicated by making \* in Table 1) required by this invention was out of range.

Ingots made from various types of pure coppers prepared in the examples were initially heat-pressure processed at 800°C to form a heat-extended plate (70 mm width x 10 mm thickness). After this heat-extended board was cooled and extended to form a cooled board

(70 mm width x 0.5 mm thickness), the board was baked/purified for 1 hour at 400°C in a vacuumed atmosphere and again cooled/extended to be made into a 35  $\mu$ m thick foil.

Also, after an ingot with a 70 mm diameter was heated/molded at 800°C of initial temperature to produce a 20 mm diameter round /230 rod, the prepared rod was made into a thin linear material (diameter = 0.9 mm) by performing a cooling/drawing process. After this linear material was purified for 1 hour at 400°C in a vacuumed atmosphere and again cooled/extended to be made into an ultra thin wire (diameter = 50  $\mu$ m).

Then, the produced foil was tested according to JIS P8115 to measure the bending resistance by counting the reciprocal bending tests applied to the foil until the test piece (15 mm wide x 110 mm long) was cut off.

To test the prepared ultra thin wire, extension process was performed on the wire to reduce the diameter from 60  $\mu$ m to the final diameter of 50  $\mu$ m, and the number of wire-breakages per 100 Kg of prepared wire was counted. The measured results are shown in Table 2.

Table 1

		(2)							(5)		(6)			(7)		(8)		
(1) 種別		純銅素材			還元性ガス組成 (容量%) (4)				脱酸素水素 富化純銅		1次脱酸素処理の 反応ガス組成 (容量%)			1次脱酸素純銅		2次脱酸素 熱処理条件		(10)
		純度 (%) (3)	[O] (ppm)	[H] (ppm)	H <sub>2</sub>	N <sub>2</sub>	Ar	CO	[O] (ppm)	[H] (ppm)	N <sub>2</sub>	Ar	CO	[O] (ppm)	[H] (ppm)	雰囲気 (9)	温度 (℃)	
(11)	本 発 明	1	99.99	3.2	0.5	0.5	—	—	99.5	0.8	0.8	100	—	—	1.0	0.6	真空	700
		2	99.99	3.5	0.5	5	—	—	95	1.0	0.8	—	100	—	1.0	0.7	Ar	700
		3	99.99	5.5	0.4	10	—	40	50	0.8	1.0	90	—	10	0.8	0.5	Ar	750
		4	99.99	5.8	0.4	15	80	—	25	0.8	1.0	—	90	10	0.8	0.5	真空	800
		5	99.99	8.3	0.5	20	—	80	—	1.0	1.8	40	40	20	1.0	1.2	Ar	800
		6	99.99	7.1	0.5	25	50	25	—	1.0	1.8	80	—	20	1.0	1.2	Ar	850
		7	99.99	7.6	0.4	30	—	60	10	1.0	2.0	—	80	20	1.0	1.3	Ar	900
		8	99.99	9.1	0.4	40	40	19	1	0.8	1.9	—	—	100	0.8	0.7	Ar	800
		9	99.99	9.6	0.4	50	50	—	—	1.0	2.2	—	—	100	1.0	0.9	Ar	800
(12)	比 較 法	1	99.99	4.8	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—
		2	99.99	3.2	0.8	—	100	—	—	3.2	0.8	—	—	—	—	—	真空	800
		3	99.99	4.8	0.4	—	—	95	5	4.5	0.4	—	—	—	—	—	Ar	800
		4	99.99	9.1	0.4	—	—	—	100	5.5	0.4	—	—	—	—	—	—	—
		5	99.99	8.8	0.4	55	—	45	—	0.9	2.4	80	—	20	0.9	1.5	Ar	800
		6	99.99	5.5	0.4	20	—	80	—	1.0	1.8	—	—	—	—	—	真空	800
		7	99.99	4.9	0.8	20	—	80	—	1.1	1.7	—	80	20	1.1	1.3	—	—
		8	99.99	8.3	0.5	20	—	80	—	1.2	1.8	—	80	20	1.2	1.3	真空	850
		9	99.99	3.9	0.6	20	—	80	—	1.0	1.8	—	80	20	1.0	1.4	真空	950

(13)

(Marked with \*: Condition was out of range of the requirements of this invention)

Key: 1) Type; 2) Pure copper material; 3) Purity; 4) Reductive gas composition (volume %); 5) Deoxidize hydrogen-rich pure copper; 6) Reaction gas composition for the first dehydrogenation process (volume %); 7) First dehydrogenated pure copper; 8) Heat processing condition for the second dehydrogenation process; 9) Atmosphere; 10) Temperature; 11) This invention; 12) Comparison method; 13) Vacuumed

Table 2

		(2)			(4)	(5)
(1) 種 別		極 低 酸 素 銅			箔材に切れが発生 するまでの往復 曲げの回数 (回)	極細線の伸線 量:100kg当りの 断線回数 (回)
		純 度 (%) <sup>(3)</sup>	(O) (ppm)	(H) (ppm)		
(6) 本 発 明 法	1	99.99	1.0	0.3	40	1.33
	2	99.99	1.0	0.3	38	1.42
	3	99.99	0.9	0.3	40	1.25
	4	99.99	1.0	0.3	42	1.37
	5	99.99	1.0	0.3	42	1.28
	6	99.99	1.0	0.2	44	1.22
	7	99.99	1.0	0.2	42	1.33
	8	99.99	0.8	0.2	46	1.19
	9	99.99	1.0	0.3	42	1.32
(7) 比 較 法	1	99.99	4.8	0.5	16	2.85
	2	99.99	3.2	0.6	20	2.56
	3	99.99	4.5	0.4	16	3.33
	4	99.99	5.5	0.4	16	3.57
	5	99.99	0.9	0.6	30	2.08
	6	99.99	1.0	0.6	30	2.50
	7	99.99	1.1	1.3	22	3.13
	8	99.99	1.2	0.8	26	2.63
	9	99.99	1.0	0.2	10	11.11

Key: 1) Type; 2) Copper containing very low oxygen; 3) Purity; 4) Number of reciprocal bending processes until foil was cut (times); 5) Number of wire-breakages per 100 Kg of extended ultra thin wire (times); 6) This invention; 7) Comparison method.

[Effectiveness of this invention]

As shown in Tables 1 and 2, the operational methods 1 - 9 of this invention could produce copper containing very low oxygen [(O) content: 1 ppm or less; (H) content: 0.3 ppm or less].

Furthermore, this copper containing a very small amount of [O] could be made into a 35  $\mu$ m thick foil and 50  $\mu$ m diameter ultra thin wire without causing noticeable foil-cutting or wire-breakage, /231 indicating the effectiveness of this invention as it will allow economical manufacturing of foil and ultra thin wire. However, as shown in Comparison examples 1 - 9, if any of the conditions required by the method based on this invention was out of range, at least one of [O] or [H] content became too high to provide satisfactory bending resistance or wire-breakage resistance. In those cases, production of 35  $\mu$ m thick foil and 50  $\mu$ m diameter ultra thin wire were practically impossible.

As explained above, the method based on this invention can produce copper containing a very small amount of oxygen [(O) content = 1 ppm or less], which is the quantity not possible with the conventional method. Since such copper contains a fairly small amount of oxygen, the copper can be made into much thinner foils or wires with excellent extension and processing characteristics than such characteristics of the products produced by the conventional method. Therefore, the method based on this invention can be

highly effective to the industry as it can provide increased integration to semiconductor devices.